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NATURAL FREEZING FOR DEWATERING OF ALUMINUM HYDROXIDE SLUDGES

J. B. Farrell, J. E. Smith Jr., R. B. Dean, E. Grossman III, and O. L. Grant

The treatment of wastewaters with aluminum sulfate results in large amounts of low-solids sludge, from which it is difficult to remove water. One method of dewatering this sludge is by natural freezing, and the authors describe the feasibility of this process herein.

TREATMENT of municipal wastewaters with aluminum sulfate is an effective means for removing phosphate from wastewaters.[1] This process, however, produces large amounts of low-solids sludge, which is extremely difficult to dewater. This study of the utilization of natural freezing for dewatering aluminum hydroxide sludges was undertaken as part of a program to determine low-cost ways for dewatering this sludge.

The use of aluminum sulfate to clarify raw water for municipal supply is commonly practiced. Disposal of the resulting sludge has recently become a major problem since Federal and state agencies are now classifying it as an industrial waste which cannot be returned to a watercourse.[2] Characteristics of aluminum hydroxide sludge from wastewater treatment and raw water treatment are nearly the same; consequently, results of this study should give a good insight into the potential of natural freezing as a means of disposing of either type of sludge.

Aluminum hydroxide sludges, when frozen slowly and completely, change character completely upon thawing. A rapidly settleable, high density precipitate is obtained. Palin,[3] Doe,[4, 5] and Webster[6] have reported their work, which demonstrated the improvement in dewatering rate of these sludges brought about by slow freezing and thawing. The latter two investigators reported on the performance of plants in which sludge was frozen by mechanical refrigeration.

Costs of mechanical refrigeration are high. In the more northern regions of the US, however, thick layers of ice are naturally produced on lakes and lagoons. Bishop and Fulton[7] have suggested a lagoon-management scheme for utilizing natural freezing. They acknowledge lack of operating experience. Doe[8] reports that Christensen in Denmark utilizes natural freezing, but information is sketchy.

This investigation was conducted to provide a foundation for rational design of a process for dewatering aluminum hydroxide sludges by natural freezing. Specific objectives of the experimental program were as follows:

1. Demonstrate whether sludge and water freeze at the same rate.
2. Set up a practical experiment in a cold location.
3. Demonstrate the utility of the freezing process in a relatively mild climate with many short cycles of freezing and thawing.
4. Demonstrate the effect on sludge properties of repeated freeze-thaw cycles in which the sludge is only partially frozen.
5. Determine whether phosphate level in the aluminum hydroxide sludge changes the effect of freezing and thawing on dewaterability.

Experimental Results

Rate of Freezing: Sludge vs. Water. Aluminum hydroxide sludges develop a structure on standing which resists free flow. It is likely that this structure inhibits natural convection, and might slow down freezing. More importantly, there could be other inhibitory effects, such as supercooling, which could retard freezing. For these reasons, an experiment was planned to compare freezing of sludge and water.

In this test, the rates of freezing of a sludge produced from waste water and a sludge produced from distilled water were compared with the rate of freezing of pure water. Sludges were made up with a molar ratio of phosphorus to aluminum of about 0.5. They were produced by dosing the water with monosodium phosphate, adding aluminum sulfate, and rapidly adjusting the pH to about 6 with sodium hydroxide. Freezing was carried out in 15-l plastic buckets. To simulate natural freezing which occurs only from the top, the buckets were insulated by covering sides and bottom with a 1.0-inch layer of glass-wool insulation and placing them inside slightly larger buckets. Freezing was carried out in a horizontal freezer held at −4 F. Twelve l of each sludge and of distilled water were charged to three buckets and freezing was commenced. Temperature was measured by means of thermocouples. Freezing was accomplished in about 70 hr. The temperature vs. time curves for all three sludges were not significantly different. Thawing at 72 F took approximately the same length of time as freezing.

A comparison of dry solids content of the sludges before and after freezing is shown below:

	Suspended Solids (g/l) Before	After
Sludge from secondary effluent	4.3	94.0
Sludge from distilled water	1.4	35.5

Solids contents after freezing and thawing were markedly increased over the initial values. Final solids con-

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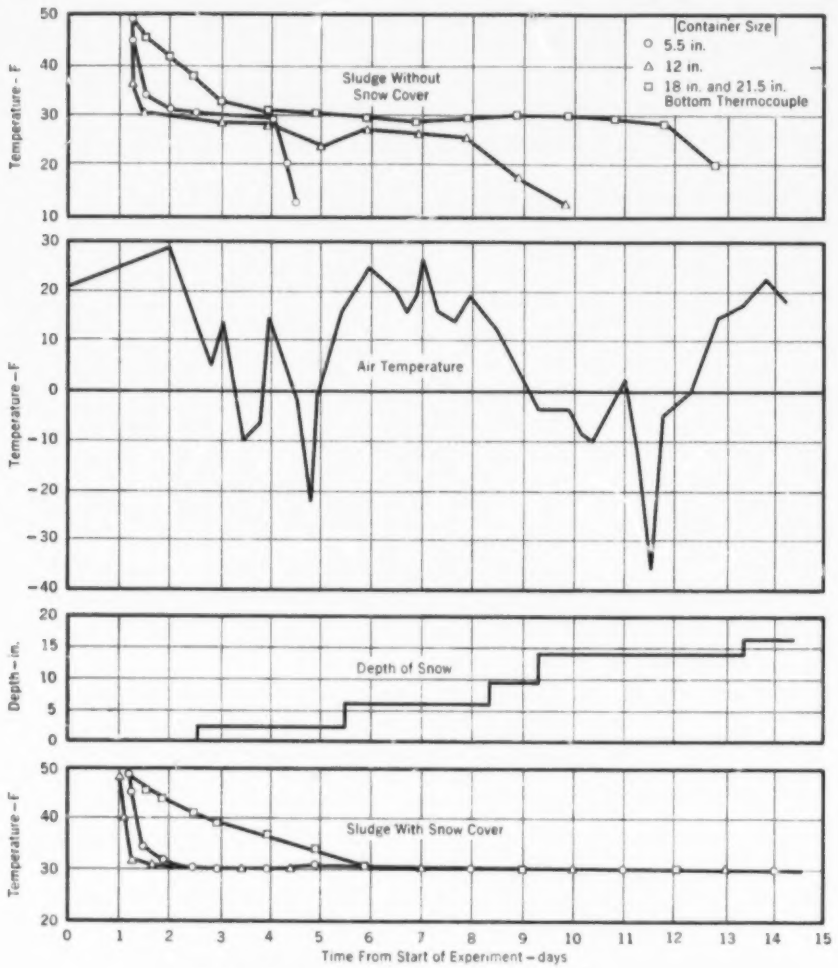

Fig. 1. Progress of Freezing in Ely Experiment

tent was not as high as is usually experienced. This may be due to the fact that both sludges were lower in solids than usual, probably because of insufficient pre-settling time.

The results of this experiment show that aluminum hydroxide sludges freeze at about the same rate as water. No unusual inhibition of freezing is experienced. Extremely thick aluminum hydroxide sludges may inhibit convection more than the sludges tested, but this effect is expected to be small (see Ely tests below). The inference of this result is important. Freezing rate information collected with water can be directly applied to sludge freezing, with provision of a small safety factor.

Freezing Experiments at Ely, Minnesota. At Ely, Minnesota, the FWPCA has a field station at which the effect of wastewater renovation on reversing eutrophication is being studied. In one step, trickling filter effluent is treated with from 100 to 200 mg/l of aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), and clarified. The availability of sludge and the cold climate at Ely made this an ideal spot for a field study.

The primary objective of this phase of the investigation was to evaluate the process under realistic field conditions. Snow cover and "lagoon" depth were seen to be a major factor in freezing. Consequently, parallel experiments were set up in which sludge was frozen in insulated containers of various depths. One set of four containers was placed on a table and kept free of snow. A second set was inserted in the ground with the top of the container at ground level, and snow cover was not removed. The containers were 5.5, 12, 18, and 21.5 in. in depth. Temperatures were recorded by means of thermocouples immersed 3 in. below the surface in all containers and 2 in. above the bottom in the two deepest containers.

Freezing data are shown for the sets with and without snow cover in Fig. 1. Complete freezing has occurred when the temperature falls significantly below 32 F. In the period shown on the graph, none of the snow-covered containers showed complete freezing, whereas all of the containers kept free of snow were completely frozen. Estimates of the time at which the containers without snow cover froze completely are given below:

Container Depth (in.)	Days for Complete Freezing
5.5	3½
12	8
18	12
21.5	12

Temperature data taken during the tests have been used to calculate the degree-days required for each container to freeze. The degree-day calculation is unconventional. Degree-days used for estimating home heating requirements are calculated by subtracting the average temperature for the day from 65 F. If the average temperature is above 65 F, degree-days are not taken as negative numbers, but are taken as zero, because there would be no heating requirement for that day. The modified degree-day used here is based on 32 F. If the average temperature for the day is above 32 F, this is calculated as a negative number and is included in any totaling of the degree-days. This is considered to be a logical procedure because temperatures above 32 F reverse the freezing process.

"Modified degree-days" required for freezing are plotted against container depth in Fig. 2. The slope of the line drawn through the data points is slightly greater than ½. A slope of ½ would be expected for freezing time as a function of depth for freezing from the top surface alone. The slightly higher slope is attributed to the relatively greater heat loss through the insulated sides of the container which occurs with the deeper (and slower freezing) containers.

Barnes [8] gives the following empirical equation for the rate of thickening of an ice sheet on quiet water already at the freezing point:

$$t + \frac{t^2}{2} = \frac{k\Delta T\theta}{L\lambda} \qquad (1)$$

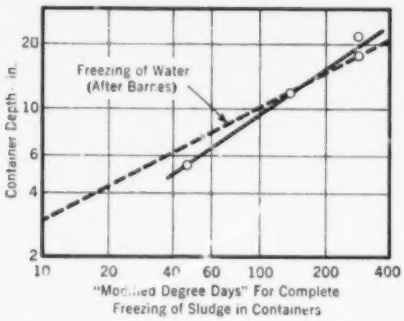

Fig. 2. Freezing Time as a Function of Container Depth for Containers Free of Snow Cover

where

t = thickness of ice sheet (cm)
k = thermal conductivity of ice (0.0057 cal/cm²sec)
ΔT = freezing temperature of ice less the air temperature (C)
θ = total exposure time (sec)
L = latent heat of freezing (80 cal/g)
λ = density of ice (0.917 g/cm³)

Note that this equation is dimensionally inconsistent and must be used with the units given.

The product, $\Delta T \cdot \theta$, in Equation 1 is the product of the time from start of freezing and the difference between the freezing point of ice and the ambient temperature. When a conversion factor for units is included, it becomes equivalent to the sum of "modified degree-days" from the start of freezing. Consequently, the equation can be presented on Fig. 2, and is shown as the dotted line on this figure. Agreement with data collected at Ely is reasonably good. Part of the discrepancy at the lower values of degree-days is due to the fact that the freezing times at Ely include the time to reduce the temperature from about 50 F to the freezing point.

The sludge used in the Ely test contained 21 g solids/l, and was thus quite thick. It was expected that, on cooling to the freezing point, natural convection would be restricted, and that temperatures at the top and bottom of the containers would be different. This kind of difference was observed for the 18 and 21.5-in. containers which contained top and bottom thermocouples.

Cooling data are shown in Fig. 3 for the 21.5-in. container kept free of snow-cover. During the period in which the bottom temperature was cooling to 32 F (3 days), there was on the average a difference of 10 F between top and bottom. Difference between air temperature and top temperature of the sludge was about 10 F during this time. This effect is attributed to the nature of this thick sludge. In the rate-of-freezing experiments noted earlier, in which water and thin sludge were frozen, differences between top and bottom temperatures in a 15-in. deep container were less than 2 F.

An estimate can be made of the effect of this non-uniform temperature on the cooling rate. If the temperature at the top surface of the sludge had been at the average temperature instead of the actual top temperature, the temperature driving force between air and sludge would have been about 15 F insteal of 10 F. This would have reduced the time to cool all of the sludge to 32 F to about 2 days instead of 3

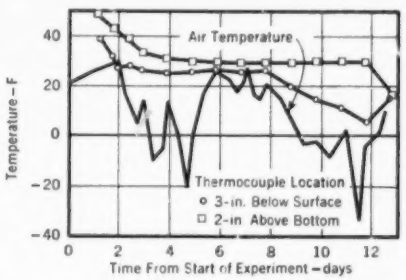

Fig. 3. Temperature Difference Between Top and Bottom When Freezing a High-Solids Sludge

days. Overall freezing time would have been reduced about 10 per cent. Thus, the freezing time of thick sludges can be estimated to be about 10 per cent higher than for water. For depths less than 21.5 in., the increase in freezing time should be less because the temperature difference between top and bottom will be less.

A summary of the effect of freezing on sludge properties is given in Table 1. At the termination of the experiment, all samples had been exposed for 2.5 months to an average ambient temperature of 8 F. Snow cover averaged 18 in. over the sludge containers in the ground. When containers were removed for thawing, they were examined to determine the fraction frozen. All containers kept free of snow were frozen solid as was the shallowest of the snow-covered containers. The deeper containers ranged from 70 per cent frozen to only 40 per cent frozen for the deepest (21.5 in.) container. Thawing was carried out by holding the containers in a room at 70 F. All were completely melted within two weeks.

The specific resistance, which indicates the resistance to filtration, was reduced about 30-fold only for those sludges which were completely frozen. Partial freezing produced about a two-fold reduction in specific resistance. Suspended solids concentration was higher for the completely frozen sludges, but here the difference between completely and partially frozen sludges was not so striking. The total organic carbon (TOC) in the supernatant was higher for completely frozen sludges. This is a matter of interest since it is clearly undesirable to resuspend in water any solids already removed as sludge. The percentage of carbon which remains in the supernatant, however, is actually very small. It is estimated that 99 per cent of the organic matter originally in the sludge remains in the sludge after the freezing-thawing sequence.

An additional experiment was run at Ely in which 1-in. increments of sludge were added to a pan exposed alongside of the set of containers frozen without snow cover. The 1-in. layers of sludge froze completely each day. Reduction in volume of the thawed sludge was slight but the improvement in filterability was as good as that obtained with the other completely frozen sludges.

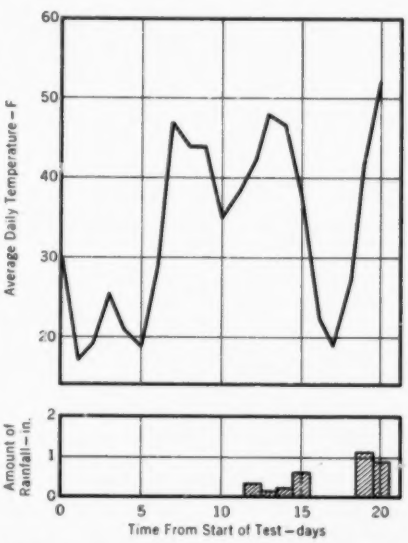

Fig. 4. Weather Conditions During Freezing Tests in Cincinnati

TABLE 1
Summarized Results of Freezing Experiments at Ely, Minnesota

Sample	Degree Frozen *per cent*	Specific Resistance $sec^2/g \times 10^{-8}$	Suspended Solids in Sludge *g/l*	TOC in Supernatant *mg/l*
Control	0	10.6	21	not measured
No snow cover (containers: 5½, 12, 18, 21½ in.)	100	0.35 av.	95 av.	177 av.
Snow cover (containers: 12, 18, 21½ in.)	40–70	5.0 av	53 av.	40 av.
Snow cover (container: 5½ in.)	100	0.37	130	175

The freezing tests at Ely showed the expected advantage of total freezing. Snow cover was demonstrated to be a critical factor. Freezing of sludges without snow cover can be predicted by known freezing relationships. Shallow layers of sludge freeze at a higher rate than deep layers. "Thick", gelatinous sludge can slow down the freezing, but the effect is minor. Layered freezing of small increments of sludge may offer a way of getting a high freezing rate of sludge with minimal interference by snow.

Freezing in a Mild Climate. Freezing was attempted at Cincinnati during the 1968–69 winter. Insulated containers 1 ft deep were filled with sludge and placed out on a roof. The objective of the experiment was to allow freezing and thawing to take place, and continually draw off any melted supernatant. This would take advantage of the frequent freeze-thaw sequences that occur in Cincinnati. In Fig. 4, the average daily temperatures on consecutive days during the test are plotted. The data show a cold spell–warm spell–short cold spell–rainy warm spell. There were additional short-term freeze-to-thaw transitions not evident from this graph of average temperatures. These proved to be of no value for removing supernatant because not enough of the frozen sludge melted to permit removal of liquid. The first warm spell, which lasted for about 3 days, melted all of the frozen sludge; about 20 per cent of the original volume could be removed as supernatant. The short cold spell which followed produced a little more freezing, but it was followed by a warm rainy period. The test was terminated because the freezing season was essentially ended and there was little hope of freezing the remainder of the sludge. The filtrability of the sludge was not improved substantially by the partial freezing and thawing which occurred in this test.

This experiment demonstrated that daily fluctuations in temperatures are of little value in producing a supernatant that can be drained away. Alternate cold and warm spells need to have a duration of two or more days. It is much better to have a low level of sludge, which can be completely frozen in the course of the winter, than too high a level. In the latter case, adverse weather could leave a sludge which had not been completely frozen. Dewaterability would then only be slightly improved.

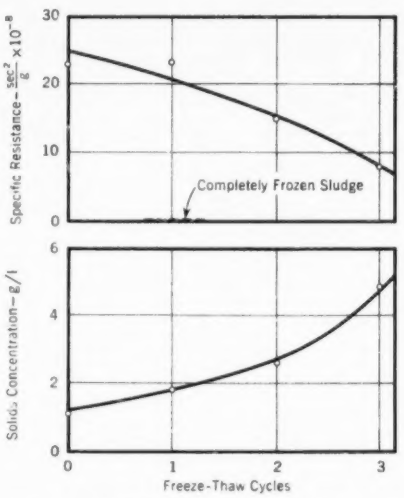

Fig. 5. Effect of Repeated Partial Freezing on Sludge Properties

The Effect of Repeated Partial Freezing and Thawing. Sludge was prepared by treatment of the secondary effluent from the Mill Creek activated sludge pilot plant in Cincinnati. Molar ratio of phosphorus to aluminum in the sludge is estimated to have been 0.5. Solids content was about 1.1 per cent. The sludge was frozen in an insulated pail, open at the top, until it was frozen for half of its depth. It was thawed and the supernatant was decanted off. The sludge was then mixed and sampled for filtrability testing and for solids determination. The sludge remaining was frozen to half its depth again and the processing described above was repeated. This was repeated for three freeze-thaw cycles. Based on three complete cycles with mixing after each cycle, it is estimated that 12 per cent of the sludge was not frozen, 38 per cent was frozen once, 38 per cent was frozen twice, and 12 per cent was frozen three times.

The data obtained with this sludge are shown in Fig. 5. Specific resistance to filtration is reduced to about one-third of its original value. Solids concentration is increased about four times. This is a substantial change and would improve filtration rates on a rotary vacuum filter about 12 times. However, as can be seen from the graph, the improvement in these properties, particularly in filtrability, is far greater with a single complete freezing. The experiment shows that even repeated partial freezing does not approach the effectiveness of a single complete freezing.

Effect of Phosphate on Sludges. Aluminum hydroxide sludges produced from wastewater can contain as much as 1.0 mole of phosphorus per mole of aluminum, whereas wastewater sludges contain very little phosphorus. It was evident that the two types of sludges qualitatively behaved in the same manner. However, it was felt that quantitative information should be obtained on the effect of phosphorus on the properties of the sludge.

Sludges with a range of phosphorus content were prepared by adding aluminum sulfate under controlled pH conditions (around 6.2) to tapwater to which known quantities of sodium dihydrogen phosphate had been added. The proportions of phosphorus to aluminum on the sludge were 0, 0.34, 0.69, and 1.04 moles P per mole of Al.

The data presented in Table 2 show that the P/Al molar ratio in the sludge does not have a large effect on the sludge density or filtrability before or after freezing. The only significant difference appears to be a better filtrability for the sludge containing no phosphorus before freezing. In all cases, slow freezing followed by thawing produced a remarkable increase in both solids content and filtrability.

The experiment demonstrated that aluminum hydroxide sludges from waterworks, which are essentially free of phosphates, should respond to freeze-

thaw cycles in virtually the same manner as aluminum hydroxide sludges laden with phosphate.

Application to Design

The results of these experiments provide a design basis for sizing of ponds for dewatering of alum sludge by natural freezing. The processing scheme proposed is to withdraw sludge from a clarifier to a thickener. Thickened sludge flows to a storage pond 15 ft in depth, where it thickens still further. In the wintertime, sludge is periodically pumped to a freezing pond, no more than 10 ft deep.

The procedure for determining relative pond size is obtained by considering a specific example. Consider a 50 mgd water plant in the vicinity of Chicago which produces 150,000 gpd of a 0.5 per cent solids sludge. In this hypothetical plant, the thickener produces 2 per cent solid sludge, and the sludge in the storage lagoon dewaters to 4 per cent solids during 12 months storage. Sludge volume to be stored in a year is 6.84 mil gal. If 10 ft of the storage is used in the year, total area requirement is 2.1 acres. The extra 5 ft in the 15-ft deep storage pond is a safety factor.

The depth of ice which can be frozen in a year is the crucial figure in deciding the area of the freezing pond. Choose a freezing depth of 5 in. In the Chicago vicinity, the "modified degree-days" based on 32 F for Dec., Jan., and Feb. have been calculated to be 450. According to Fig. 2, 25 degree-days are required to freeze a 5-in. layer. A maximum of eighteen 5-in. layers can be frozen by 450 degree-days, or 90 in. This is almost certainly an overestimate, since extra time must be allowed to make sure that the sludge is completely frozen. In addition, snow cover has not been considered. The effects of snow cover can be minimized by plowing off the snow, by not pumping sludge for freezing when snow is anticipated, and, if snow falls on sludge not yet frozen, by pumping sludge on top of it. This will partially melt it, and will reduce its thickness and its insulating properties. To compensate for these anticipated difficulties, the 90-in. figure is reduced by 50 per cent to 45 in. To freeze 6.84 mil gal of sludge would require 5.6 acres. Depth of the lagoon should probably be about 8 ft. Excess capacity, if desired, is provided by more area. Greater depth provides extra capacity when the sludge is frozen in thinner layers.

Conclusion

This study has attempted to provide basic information essential to adequately design facilities for dewatering aluminum hydroxide sludges by natural freezing. Important findings are:

(1) Freezing rate of aluminum hydroxide sludges is similar to freezing rate of water. The sludges may take about 10 per cent longer to freeze because natural convection is reduced during the stage when the liquid is being cooled to the freezing point. Freezing rate of sludges correlated adequately with literature data on water freezing.

TABLE 2

Effect of Freeze-Thaw Cycle on Properties of Aluminum Hydroxide Sludges with Varying Amounts of Phosphate

Nominal P/Al Molar Ratio	Before Freezing		After Freezing	
	Solids Content g/l	Specific Resistance $sec^2/g \times 10^{-9}$	Solids Content g/l	Specific Resistance $sec^2/g \times 10^{-9}$
0	3.20	10	176	0.04
0.34	2.50	19	168	0.06
0.69	3.20	16	180	0.06
1.04	2.84	16	178	0.07

(2) Snow cover is a serious obstacle to a freezing facility, even in extremely cold climates. Proper management can reduce the problem: by freezing in thin layers, by not putting out sludge when snow is expected, by melting the snow with a water flush or by layering out more sludge, and by plowing off the snow.

(3) Sludge dewaterability and solids content are dramatically increased by slow freezing and thawing, provided the freezing is complete. Repeated partial freezing increases dewaterability and solids content but to a much smaller degree. It appears a much sounder approach to freeze completely just once, even if it means more management of the freezing facility.

(4) Freezing in a mild climate, such as Cincinnati's, could be successful only if thin layers of sludge, in the order of an inch, are applied at a time. This could result in excessive management costs.

(5) The filtrability and solids content of aluminum hydroxide sludges is affected only slightly by phosphorus contents ranging from zero to 1.0 mole of phosphorus per mole of aluminum.

The information collected in this investigation permits a rational approach to freezing pond design. Large uncertainties still remain in the prediction of pond sizes, mostly because the success in overcoming the problems created by snow cover cannot be accurately predicted. Further development of the natural freezing method for dewatering alum sludges will likely come about from pilot-scale tests of freezing pond management during a winter.

Acknowledgment

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